

(Adopted March 6, 1987)(Amended April 3, 1987)(Amended August 3, 1990)
(Amended December 7, 1990) (Amended August 2, 1991)(Amended July 10, 1992)
(Amended May 13, 1994)(Amended November 17, 2000)(Amended November 9, 2001)
(Amended July 11, 2003)(Amended July 9, 2004)

March 15, 2005

PROPOSED AMENDED RULE 1162 POLYESTER RESIN OPERATIONS

(a) Applicability

This rule shall apply to all polyester resin operations that fabricate, rework, repair, or touch-up products for commercial, military, or industrial use including, but not limited to, boats, tubs, pools, shower enclosures, spas, bathroom fixtures, jigs, tools, molds, building panels, air pollution control equipment, sewage treatment equipment, storage tanks, transportation parts, automotive, aircraft, and aerospace components, and other industrial and consumer products.

(b) Definitions

For the purpose of this rule, the following definitions shall apply:

- (1) AIR-ASSISTED AIRLESS SPRAY is a coating application system in which the coating fluid is supplied to the gun under fluid pressure and air is combined at the spray cap.
- ~~(2)~~(4) CLOSED MOLDING SYSTEM is a method of fabricating composite parts by placing composite materials in a confining mold cavity and applying pressure and/or heat.
- ~~(3)~~(2) CORROSION-RESISTANT MATERIALS are polyester resin materials used to make products for corrosion resistant applications such as tooling, fuel or chemical tanks, boat hulls, pools and outdoor spas.
- (4) ELECTROSTATIC APPLICATION is charging of atomized coating droplets for deposition to a grounded substrate by electrostatic attraction.
- ~~(5)~~(3) EXEMPT COMPOUND is as defined in Rule 102.
- ~~(6)~~(4) FIBER REINFORCEMENT MATERIALS are multifilament of glass or other fibrous materials such as, carbon, boron, metal and amid polymers, which are used to reinforce plastic.
- ~~(7)~~(5) FIBER REINFORCED PLASTIC OR COMPOSITE (FRP/C) MATERIALS is a mixture of polyester resin and fiber reinforcement materials.

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~~(8)(6)~~ FILLER is a finely divided inert (non-VOC) material, which may be added to the resin to enhance its mechanical properties and extend its volume. Resin fillers include, but are not limited to, silica, carbon black, talc, mica and calcium carbonate.

~~(9)(7)~~ FILLED POLYESTER RESIN MATERIAL is a material formulated by adding compatible filler(s) to polyester resin material(s).

~~(10)(8)~~ FIRE RETARDANT MATERIALS are polyester resin materials used to make products that are resistant to flame or fire.

~~(11)(9)~~ FLOWCOATER is a nonatomizing application technique of applying resins and gel coats to an open mold with a fluid nozzle in a fan pattern with no air supplied to the nozzle.

~~(12)(40)~~ GEL COAT is a thermosetting polyester resin surface coating, either pigmented or clear, that provides a cosmetic enhancement and improves resistance to degradation from exposure to the elements.

~~(13)(41)~~ GENERAL PURPOSE POLYESTER RESINS are resin materials that are not corrosion resistant, fire retardant, high strength, or gel coats.

~~(14)(42)~~ HAND LAY-UP is a hand application technique of composite materials using a bucket and a paint brush or a paint roller, or other hand held method of application.

~~(15)~~ HIGH-VOLUME, LOW-PRESSURE (HVLP) SPRAY is a coating application system which is operated at air pressures between 0.1 and 10 pounds per square inch gauge (psig) measured dynamically at the center of the air cap and at the air horns.

~~(16)(43)~~ HIGH-STRENGTH MATERIALS are polyester resins which have casting tensile strength of 10,000 psi or more and which are used for manufacturing of high performance boats and skis.

~~(17)(44)~~ LAMINATION RESINS are orthophthalate, isophthalate and dicyclopentadiene (DCPD) resins which are used in composite system made of layers of reinforcement fibers and resins, such as in boat fabrication.

~~(18)(45)~~ MARBLE OR CULTURED RESINS are orthophthalate and modified acrylic isophthalate resins, which are designed for the fabrication of cast products, such as vanities.

~~(19)(46)~~ MONOMER is a volatile organic compound that partially combines with itself, or other similar compounds, by a cross-linking reaction to become a

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part of the cured resin. Monomers include, but are not limited to, styrene and methyl methacrylate.

~~(20)~~(47) MONOMER PERCENT BY WEIGHT OF A RESIN is the weight of the monomer, divided by the weight of the polymer.

~~(21)~~(48) MONOMER PERCENT BY WEIGHT OF A FILLED RESIN AS APPLIED is the weight of the monomer, divided by the weight of the polymer and filler(s).

~~(22)~~(49) NONATOMIZING SPRAY APPLICATION TECHNIQUE OF RESIN is any application technique in which resin flows from the applicator, in a steady and observable coherent flow, without droplets, for a minimum distance of three (3) inches from the applicator orifices.

~~(20) NONATOMIZING SPRAY APPLICATION TECHNIQUE OF GEL COAT is the use of application equipment to apply gel coat where test results and parameters document that the use of this application equipment results in VOC emissions that are no greater than the VOC emissions specified in Attachment A—Unified Emission Factors For Open Molding of Composites table of this rule.~~

~~(23)~~(21) OPEN MOLDING SYSTEM is a method of fabricating composite parts by applying gel coats, resins, fibers, and other composite materials on an open mold using either hand lay-up or spray-up applications.

~~(24)~~(22) POLYESTER is a polymer of ester molecules, which are formulated by the reaction of an acid and an alcohol and linked together by the ester linkages.

~~(25)~~(23) POLYESTER RESIN MATERIALS are polyester resins, such as isophthalic, orthophthalic, halogenated, bisphenol A, vinyl ester, or furan resins; cross-linking agents; catalysts; gel coats; inhibitors; accelerators; promoters; and any other material containing VOC used in polyester resin operations.

~~(26)~~(24) POLYESTER RESIN OPERATIONS fabricate, rework, repair, or touch-up products for commercial, military, or industrial use by mixing, pouring, hand laying-up, impregnating, injecting, forming, winding, spraying, and/or curing by using polyester resin materials.

~~(27)~~(25) POLYMER is a chemical compound, such as polystyrene, comprised of a large number of chemical units (monomer) composed of identical cross-linking groups, such as styrene.

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~~(28)~~~~(26)~~ PRESSURE-FED ROLLER is a fabric roller that is fed with continuous supply of catalyzed resins from a mechanical fluid pump.

~~(29)~~~~(27)~~ PRIMER GEL COAT is gel coat which is used to coat the surface of composite parts, prior to top-coat painting, for automotive, aerospace, marine and home building industries.

~~(30)~~~~(28)~~ PULTRUSION is a process where continuous roving strands are moved through a strand-tensioning device into a resin bath for impregnation and then passed through a heated die for curing.

~~(31)~~~~(29)~~ REPAIR is that portion of the fabrication process that requires the addition of polyester resin materials to portions of a previously fabricated product in order to mend damage.

~~(32)~~~~(30)~~ RESIN is any thermosetting polyester resin, which is used to encapsulate and bind together reinforcement fibers and /or fillers in the formulation of composite materials.

~~(33)~~~~(31)~~ RESIN IMPREGNATOR is a mechanical nonatomizing composite materials application technique in which fiber reinforcement is saturated with resins in a controlled ratio for each specific composite product.

~~(34)~~~~(32)~~ SOLID SURFACE RESINS are resins, which are used without gel coats to fabricate homogenous solid surface products.

~~(35)~~~~(33)~~ SPECIALITY GEL COATS are gel coats which are used in conjunction with fire retardant, corrosion resistant or high-strength materials.

~~(36)~~~~(34)~~ THERMOSET POLYESTER RESIN is a resin material that undergoes a chemical reaction during curing and can not be reshaped.

~~(37)~~~~(35)~~ TOUCH-UP is that portion of the process that is necessary to cover minor imperfections.

~~(38)~~~~(36)~~ TUB/SHOWER RESINS are dicyclopentadiene (DCPD) resins, along with orthophthalate and isophthalate resins, which are used to fabricate bathware products.

~~(39)~~~~(37)~~ VAPOR SUPPRESSANT is a wax substance added to resin for the purpose of forming a layer on the surface of the resin while it is curing and minimize the outward diffusion of monomer vapor into the atmosphere.

~~(40)~~~~(38)~~ VAPOR SUPPRESSED RESIN (VSR) is a polyester resin material which contains additives to reduce VOC evaporation loss to less than fifty (50) grams per square meter of surface area as determined and certified by resin manufacturers.

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(41)(39) VOLATILE ORGANIC COMPOUND (VOC) is as defined in Rule 102.

(c) Requirements

(1) Application Techniques

(A) Except for gel coats, effective July 1, 2002, a person shall not apply any resin materials to an open mold surface unless one of the following nonatomizing application techniques is used and operated according to the operating procedure specified by the equipment manufacturer:

- (i) Nonatomizing Spray Application Technique; as defined in paragraphs (b)(19) and (b)(20)
- (ii) Flowcoaters;
- (iii) Pressure-Fed Rollers;
- (iv) Resin Impregnators;
- (v) Hand Lay-up Applications; or
- (vi) Other nonatomizing application techniques which are approved in writing by the Executive Officer, CARB, and U.S. EPA, as having similar emission reduction efficiencies.

(B) Effective July 1, 2005, an operator shall not apply gel coat materials to an open molding surface unless one of the following nonatomizing application techniques is used and operated according to the operating procedure specified by the equipment manufacturer; of clauses (c)(1)(A)(i) through (c)(1)(A)(vi) is used and operated according to the operating procedure specified by the equipment manufacturer. The operator using a nonatomizing spray application technique to apply gel coat shall only operate spray equipment at or below the application spray pressure for that equipment where test results demonstrate that the use of spray equipment results in VOC emissions that are no greater than the VOC emissions specified in Attachment A—Unified Emission Factors For Open Molding of Composites table of this rule. The operator shall provide to the Executive Officer upon request, test results and parameters, such as spray application pressure, that demonstrate compliance with this requirement. The test to determine the VOC emissions from the nonatomizing spray

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~~application technique must be calculated utilizing test methods approved by the Executive Officer in accordance with U.S. EPA guidelines.~~

- ~~(i) Any nonatomizing application technique listed under subparagraph (c)(1)(A);~~
- ~~(ii) Air-Assisted Airless Spray;~~
- ~~(iii) Electrostatic Attraction; or~~
- ~~(iv) High-Volume, Low-Pressure (HVLN)~~

(2) Material Requirements

- (A) A person shall not use polyester resin material in an open molding system, which has a monomer content in excess of the limits specified in the following Table.

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Polyester Resin Materials	Monomer Percentage by Weight as Applied	
	Prior to 11-09-2001	Current Limits
Clear Gel Coat	50	-
For Marble Resins	-	40
For Other Resins	-	44
Pigmented Gel Coat	45	-
White and Off White	-	30
Non-White	-	37
Primer	-	28
Specialty Gel Coats	-	48
General Purpose Resin	35	-
Marble Resins	-	10 or (32 % as supplied, no fillers)
Solid Surface Resins	-	17
Tub/Shower Resins	-	24 or
Lamination Resins	-	(35 % as supplied, no fillers) 31 or (35 % as supplied, no fillers)
Others	-	35
Fire Retardant Resin	42	38
Corrosion Resistant Resin	48	48
High Strength Resin	48	40

(B) Composite operations that are also subject to Rule 1132 and have elected to comply under the alternative compliance option specified in paragraph (d)(1) of Rule 1132, shall comply with the July 1, 2002, monomer content requirements of subparagraph (c)(2)(A) on January 1, 2002.

(C) Effective July 1, 2002, a person shall not apply to an open molding system any tub/shower polyester resin material unless all the applied resin material is vapor suppressed.

(3) Process Requirements

(A) A person shall not operate a closed molding system, unless the weight loss of polyester resin materials during polymerization is less than four (4) percent.

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- (B) Until July 1, 2002, in lieu of using resins that comply with the monomer content requirements of subparagraph (c)(2)(A), a person may use a vapor suppressed resin, provided the weight loss from VOC emissions does not exceed fifty (50) gram per square meter of exposed surface area during resin polymerization.
 - (C) A person shall not perform a pultrusion operation, unless wet-out baths are covered except for 18 inches from the exit of the bath to the die. The weight loss of polyester resin materials during polymerization shall be less than three (3) percent in a pultrusion operation.
 - (4) Notwithstanding the requirements specified in paragraph (c)(1), a person may perform touch-up and repair using a hand-held spray gun which has a container for gel coat or resin as part of the gun.
 - (5) Any person processing polyester resin materials and any other VOC-containing materials shall keep these materials in closed containers except when filling or emptying the container.
 - (6) Solvent cleaning of application equipment, parts, products, tools, machinery, equipment, general working areas, and the storage and disposal of VOC-containing materials used in cleaning operations shall comply with Rule 1171 - Solvent Cleaning Operations.
- (d) **Control Equipment**
- In lieu of complying with the requirements of subdivision (c), a person may install and operate an emission control system which has an overall capture and control efficiency of 90 percent or more on a mass basis, as approved by the Executive Officer.
- (e) **Recordkeeping Requirements**
- (1) A person subject to the provisions of this rule shall maintain daily records. Alternatively, records may be kept on a monthly basis provided the polyester resin process or equipment is not subject to a daily production limit or daily VOC limit in any applicable District rule(s) or permit(s). Such records shall be made available to the Executive Officer's designee upon request and shall be kept for not less than two years. The records shall contain:

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- (A) The type of the nonatomizing application technique(s) used, manufacturer's name, and the records of the fluid tip pressure calibration as specified by the manufacturer;
 - (B) The manufacturer's name, the type and amount of each of the polyester resin materials used; and the weight (in percent) of monomer for all polyester resin materials and filler(s). If VOC-containing materials are added to the polyester resin, the amount of VOC-containing materials, in grams, and the VOC content in grams per liter, of VOC-containing materials;
 - (C) Certification of Analysis from the resin manufacture(s) to verify that all the applied tub/shower resin materials are vapor suppressed; and
 - (D) For closed-mold and pultrusion systems, the weight loss (in percent) of polyester resins materials for each application.
- (2) Records for cleaning solvents subject to Rule 1171 - Solvent Cleaning Operations shall be maintained pursuant to Rule 109.
- (3) Any person using an emissions control system as a means of complying with this rule shall maintain daily records of all key system parameters, including hours of operation, temperatures, pressures and flow rates, that are necessary to ensure control efficiency requirements.
- (f) Test Methods and Procedures
- The following test methods and procedures shall be used to determine compliance with this rule. Other applicable test methods may be used if they are determined to be equivalent and approved in writing by the Executive Officer, the California Air Resources Board and the U.S. Environmental Protection Agency.
- (1) Determination of VOC Content of VOC-Containing Materials
 - (A) U.S. EPA Method 24 - Determination of Volatile Matter Content, Water Content, Density Volume Solids, and Weight Solids of Surface Coating.
 - (B) District Methods 302 and 303 – Determination of Exempt Compounds.
 - (C) District Method 304- -Determination of Volatile Organic Compounds (VOCs) in Various Materials, or any other applicable method approved by the US Environmental Protection Agency, California Air Resources Board, and the SCAQMD.

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- (D) District Method 309 – Determination of the Weight Loss of Polyester Resin Materials.
- (E) District Method 312 – Determination of the monomer content of Polyester Resin Materials.
- (F) District Method 313 – Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry.
- (2) Determination of Efficiency of Emission Control System
 - (A) The capture efficiency of an emission control system shall be determined by verifying the use of a Permanent Total Enclosure (PTE) and 100 % capture efficiency as defined by U.S. EPA Method 204 “Criteria for and Verification of a Permanent or Temporary Total Enclosure.” Alternatively, if a U.S. EPA Method 204 defined PTE is not employed, capture efficiency shall be determined using a minimum of three sampling runs subject to data quality criteria presented in U.S. EPA technical guidance document “Guidelines for Determination Capture Efficiency, January 9, 1995.” Individual capture efficiency test runs subject to the U.S. EPA technical guidelines shall be determined by:
 - (i) The Temporary Total Enclosure (TTE) approach of U.S. EPA Method 204 through 204F; or
 - (ii) The District “Protocol for Determination of Volatile organic Compounds (VOCs) Capture efficiency.”
 - (B) The efficiency of the control device and the VOC content measured and calculated as carbon in the control device exhaust gases shall be determined by U.S. EPA's Test Method 18, or Air Resources Board (ARB) Method 422 for the determination of emissions of Exempt Compounds and U.S. EPA's Test Methods 25, 25A, District Method 25.1 for the determination of Total Gaseous Non-Methane Organic Emissions as Carbon, or District Method 25.3 for the determination of Low Concentration Non-Methane Non-Ethane Organic Compound Emissions from Clean Fueled Combustion Sources, as applicable.
 - (C) The overall efficiency of an emission control system shall be determined using the following equation:
Overall Efficiency
$$= (\text{Capture Efficiency}) \times (\text{Control Equipment Efficiency})/100$$

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(g) Alternative Compliance Option

A person may use alternative application processes and materials to those listed in paragraphs (c)(1) and (c)(2) provided they result in equivalent VOC emissions and are approved in writing by the Executive Officer, CARB and U.S. EPA.

Unified Emission Factors for Open Molding of Composites

July 23, 2001

Emission Rate in Pounds of Styrene Emitted per Ton of Resin or Gelcoat Processed

Styrene content in resin/gelcoat, % ⁽¹⁾	<33 ⁽²⁾	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	>50 ⁽²⁾
Manual	0.126 x %styrene x 2000	83	89	94	100	106	112	117	123	129	134	140	146	152	157	163	169	174	180	((0.286 x %styrene) - 0.0529) x 2000
Manual w/ Vapor Suppressed Resin VSR ⁽³⁾	Manual emission factor [listed above] x (1 - (0.50 x specific VSR reduction factor for each resin/suppressant formulation))																			
Mechanical Atomized	0.169 x %styrene x 2000	111	126	140	154	168	183	197	211	225	240	254	268	283	297	311	325	340	354	((0.714 x %styrene) - 0.18) x 2000
Mechanical Atomized with VSR ⁽³⁾	Mechanical Atomized emission factor [listed above] x (1 - (0.45 x specific VSR reduction factor for each resin/suppressant formulation))																			
Mechanical Atomized Controlled Spray ⁽⁴⁾	0.130 x %styrene x 2000	86	97	108	119	130	141	152	163	174	185	196	207	218	229	240	251	262	273	0.77 x ((0.714 x %styrene) - 0.18) x 2000
Mechanical Controlled Spray with VSR	Mechanical Atomized Controlled Spray emission factor [listed above] x (1 - (0.45 x specific VSR reduction factor for each resin/suppressant formulation))																			
Mechanical Non-Atomized	0.107 x %styrene x 2000	71	74	77	80	83	86	89	93	96	99	102	105	108	111	115	118	121	124	((0.157 x %styrene) - 0.0165) x 2000
Mechanical Non-Atomized with VSR ⁽³⁾	Mechanical Non-Atomized emission factor [listed above] x (1 - (0.45 x specific VSR reduction factor for each resin/suppressant formulation))																			
Filament application	0.184 x %styrene x 2000	122	127	133	138	144	149	155	160	166	171	177	182	188	193	199	204	210	215	((0.2746 x %styrene) - 0.0298) x 2000
Filament application with VSR ⁽³⁾	0.120 x %styrene x 2000	79	83	86	90	93	97	100	104	108	111	115	118	122	125	129	133	136	140	0.65 x ((0.2746 x %styrene) - 0.0298) x 2000
Gelcoat Application	0.445 x %styrene x 2000	294	315	336	356	377	398	418	439	460	481	501	522	543	564	584	605	626	646	((1.03646 x %styrene) - 0.195) x 2000
Gelcoat Controlled Spray Application ⁽⁴⁾	0.325 x %styrene x 2000	215	230	245	260	275	290	305	321	336	351	366	381	396	411	427	442	457	472	0.73 x ((1.03646 x %styrene) - 0.195) x 2000
Gelcoat Non-Atomized Application ⁽⁸⁾	SEE Note 9 below	196	205	214	223	232	241	250	259	268	278	287	296	305	314	323	332	341	350	((0.4506 x %styrene) - 0.0505) x 2000
Covered-Cure after Roll-Out	Non-VSR process emission factor [listed above] x (0.80 for Manual <or> 0.85 for Mechanical)																			
Covered-Cure without Roll-Out	Non-VSR process emission factor [listed above] x (0.50 for Manual <or> 0.55 for Mechanical)																			

Emission Rate in Pounds of Methyl Methacrylate Emitted per Ton of Gelcoat Processed

MMA content in gelcoat, % ⁽⁶⁾	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	≥20
Gel coat application ⁽⁷⁾	15	30	45	60	75	90	105	120	135	150	165	180	195	210	225	240	255	270	285	0.75 x %MMA x 2000

Notes

- 1 Including styrene monomer content as supplied, plus any extra styrene monomer added by the molder, but before addition of other additives such as powders, fillers, glass,...etc.
- 2 Formulas for materials with styrene content < 33% are based on the emission rate at 33% (constant emission factor expressed as percent of available styrene), and for styrene content > 50% on the emission rate based on the extrapolated factor equations; these are not based on test data but are believed to be conservative estimates. The value for "% styrene" in the formulas should be input as a fraction. For example, use the input value 0.30 for a resin with 30% styrene content by wt.
- 3 The VSR reduction factor is determined by testing each resin/suppressant formulation according to the procedures detailed in the *CFA Vapor Suppressant Effectiveness Test*.
- 4 SEE the *CFA Controlled Spray Handbook* for a detailed description of the controlled spray procedures.
- 5 The effect of vapor suppressants on emissions from filament winding operations is based on the *Dow Filament Winding Emissions Study*.
- 6 Including MMA monomer content as supplied, plus any extra MMA monomer added by the molder, but before addition of other additives such as powders, fillers, glass,...etc.
- 7 Based on gelcoat data from *NMMA Emission Study*.
- 8 SEE the July 17, 2001 EECS report *Emission Factors for Non-Atomized Application of Gel Coats used in the Open Molding of Composites* for a detailed description of the non-atomized gelcoat testing.
- 9 Use the equation ((0.4506 x %styrene) - 0.0505) x 2000 for gelcoats with styrene contents between 19% and 32% by wt.; use the equation 0.185 x %styrene x 2000 for gelcoats with less than 19% styrene content by wt.

UEF unified factors table revised July 23 '01.xls